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Theoretical insights into structural–electronic relationships and relative stability of the Cu-, Al- and O-terminated $CuAlO_2(0001)$ surfaces

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Geometrical, electronic, energetic and thermodynamic properties of the Cu-, Al- and O-terminated $CuAlO_2(0001)$ surfaces have been studied by first-principles density functional theory (DFT) calculations. The atomic displacements and surface relaxations of four different terminations were taken into account. According to the results of the surface electronic properties, the Cu-terminated and Al-terminated $CuAlO_2(0001)$ surfaces are metallic, and the OI and OII surfaces present the p-type semiconductor surfaces. The surface energies and thermodynamic stability of $CuAlO_2(0001)$ surfaces have been analyzed, indicating that the OI surface is the thermodynamically most stable termination.

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1. Introduction

Extensive research efforts aimed to develop low-resistive p-type transparent conducting oxides (TCOs) have became a very attractive field due to their outstanding physical and chemical properties after the delafossite-structured $CuAlO_2$ films were firstly reported [1]. The p-type TCOs are important materials with a wide range of potential applications in light emitting diodes (LED) [2], functional p–n heterojunctions for solar cells [3], flat-panel displays [4], touch screens [5], diluted magnetic semiconductors [6], ozone sensors [7], photocatalytic hydrogen generators [8], thermoelectric converters [9], infrared reflective coatings [10], and other transparent optoelectronic devices [11,12]. Currently, the Cu-based p-type TCOs are widely studied, e.g., $CuM^{IIIA}X_2^{VI}$, $CuM^{IIIB}X_2^{VI}$ (M^{IIIA} = Al, Ga, In; M^{IIIB} = Sc, Y, La; X^{VI} = O, S, Se, Te) [13–23]. However, the conduction mechanism of p-type TCOs and the lower conductivity of p-type compared with that of n-type conducting oxides are still challenging problems.

During the last few years, numerous studies related to the origin and improvement of p-type conductivity have been developed. The hybridized antibonding between Cu d_{z^2} orbitals and O sp hybrids at the top of the valence band is responsible for p-type conductivity by using the extended Hückel method [24]. Tate et al. [25] reported the origin of p-type conduction in $CuAlO_2$ and found that the conduction mechanism was charge transport in the valence band and the holes were thermally activated at 700 meV above the valence band maximum. Moreover, the smaller Cu–Cu distances in Cu-based TCOs could cause an increase in intrinsic conductivity [26]. In a word, though the relation between geometrical/electronic structure and conductivity has more work to do, the Cu^+ cations having closed d-shells weaken ionic interactions of metal–oxygen bonding, which therefore accelerates the development of Cu-based p-type TCOs. Scanlon et al. [3] used DFT corrected for on-site Coulombic interactions to study $Cu^IM^{III}O_2$ (M^{III} = Al, Cr, Sc, Y) delafossite transparent conducting oxides, and concluded the improved conductivity associated with covalent interactions between the M^{III} ion and the O 2p states. However, the small polaron conduction mechanism linked with hole hopping between Cu sites limits the mobility in $CuAlO_2$ [27]. Hence, the defect mechanisms induced the decrease of trapped holes have attracted attention. Ingram et al. [4] reported that a defect complex $(Al_{Cu}^{\bullet\bullet}2O_i'')''$ was served as an acceptor and contacted with conductivity, but Scanlon and Watson found that Cu_{Al} and V_{Cu} formation were mainly responsible for the conductivity in

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$CuAlO_2$ [12]. Furthermore, the heavily doped p-type $CuAlO_2$ having two-dimensional nested Fermi surfaces exhibits possibly transparent superconductivity [28], and 0.2–0.3 hole doping in $CuAlO_2$ results in transition to high-T_c superconductor with $T_c \simeq 50$ K [29]. Recently, the N impurity states at the top of valence band maximum enhancing the p-type conductivity of N-doped $CuAlO_2$ has been concluded [30]. Even now, the design and fabrication of low-resistive Cu-based p-type TCOs remain unfinished.

On the other hand, as the p-type transparent conducting films, prospective studies of physical and chemical properties in $CuAlO_2$ surfaces are in great demand. Despite the wealth of experimental studies on $CuAlO_2$ films [31–35], there still lacks a comparison with theoretical work on surfaces. Moreover, due to the intrinsic limitations of experimental precision and technical difficulty, theoretical calculations supported by the basis of first-principles within density functional theory (DFT) have attracted a great deal of attention of numerous scientists. The epitaxial monolayer graphene on Ru(0001) [36] and SiC(0001) [37] surfaces, the adsorption energetics on Se-modified Ru(0001) [38] and Al-terminated α-Al_2O_3 (0001) [39] surfaces, the surface magnetism [40], the surface growth [41] and the surface catalysis [42], etc. are all solved perfectly, indicating that we can use the same method to investigate $CuAlO_2$ surfaces. Taking into account the importance of surface properties for thin films, understanding the physical and chemical properties of $CuAlO_2$ surface states is all-important for the future development of high quality $CuAlO_2$ films.

In this paper, different atom-terminated models including Cu-, Al- and O-terminated $CuAlO_2$(0001) surfaces have been taken into account. The surface relaxations, surface electronic structures, surface energies and thermodynamic stability of $CuAlO_2$(0001) surfaces in all their terminations have been studied by first-principles calculations. The rest of the work is organized as follows: the computational approach used to calculate $CuAlO_2$(0001) surfaces and the corresponding surface models are shown in Section 2. In Section 3, we study the calculated results, including geometrical, electronic, energetic and stable properties of $CuAlO_2$(0001) surfaces. Finally, our conclusions are presented in Section 4.

2. Computational details and models

2.1. Computational methods

The periodic DFT calculations were performed using the plane-wave pseudopotential method implemented in the CASTEP code [43]. The ultrasoft pseudopotential and the local density approximation (LDA) with the Ceperley–Alder–Perdew–Zunger (CA–PZ) form [44] were used to describe the exchange and correlation potentials. According to the Monkhorst–Pack scheme [45], the *k*-point meshes in Brillouin zone were 4 × 4 × 4, 4 × 4 × 2, 6 × 6 × 6 and 6 × 6 × 1 for bulk Cu_2O, Al_2O_3, $CuAlO_2$ and $CuAlO_2$(0001) surfaces in all their terminations, respectively, and the plane-wave cutoff energy was set to 380 eV. The Cu $3d^{10}4s^1$, Al $3s^23p^1$ and O $2s^22p^4$ electrons were treated as valence electrons. The convergence thresholds for total energy, maximum force, maximum stress, and maximum displacement were less than 5×10^{-6} eV/atom, 0.01 eV/Å, 0.02 GPa and 5×10^{-4} Å, respectively.

2.2. $CuAlO_2$(0001) surfaces

Before constructing the surface models, we optimized the bulk structures and energies of cubic Cu_2O, trigonal Al_2O_3 and $CuAlO_2$ shown in Fig. 1 in their most stable phases at ambient conditions by the same computational methods and convergence thresholds to (1) check the applicability and accuracy of computational methods, (2) prove the repeatability of our approach to be consistent with experimental results, not only the bulk properties, but also the surface properties, and (3) provide available data for surface energies and stability calculations. The space groups of cubic Cu_2O, trigonal Al_2O_3 and $CuAlO_2$ are $Pn\bar{3}m$ with a simple cubic lattice entitled cuprite structure, $R\bar{3}c$ and $R\bar{3}m$ with a hexagonal (conventional) or a rhombohedral (primitive) unit cell. The calculated lattice parameters are $a = 4.1639$ Å for cubic Cu_2O,

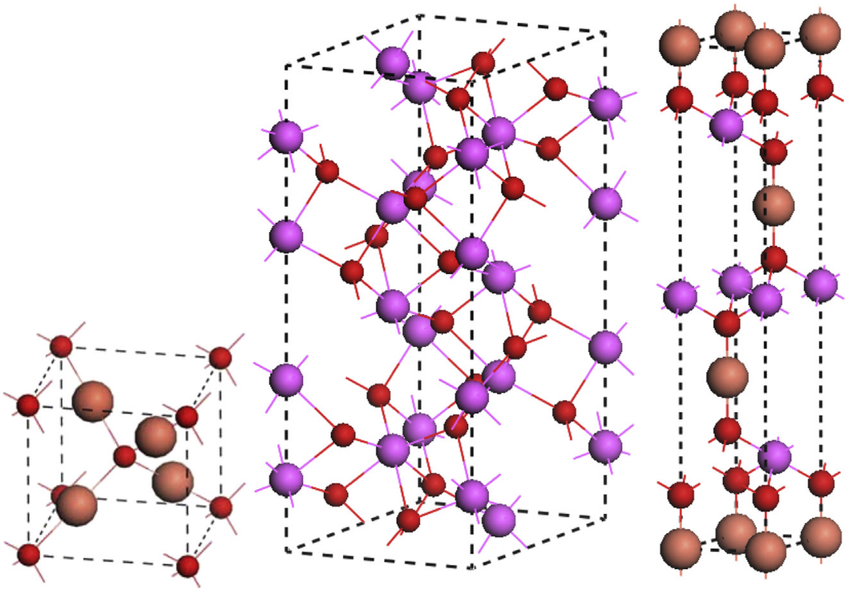

Fig. 1. Crystal structures of (a) cubic Cu_2O, (b) trigonal Al_2O_3, (c) trigonal $CuAlO_2$. The O, Al and Cu atoms are represented as red (small), purple (medium) and red copper (large) spheres, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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